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Applicability of Existing Methods for the Determination of the Biochem. Oxygen Demand (BOD) of Incinerator Quench Water

Bureau of Solid Waste Management

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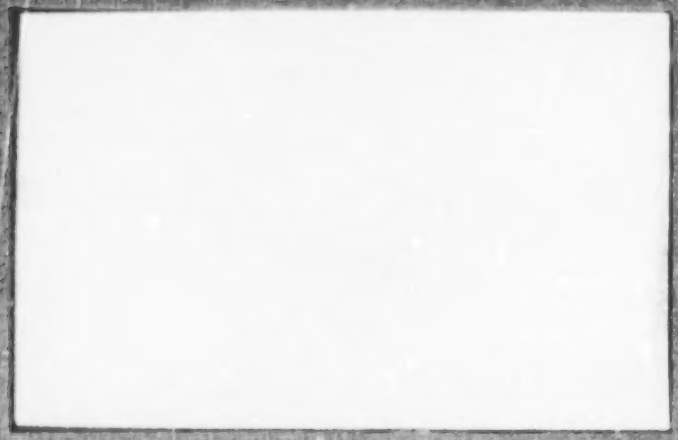

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***In this report quench water refers to that water which has been employed by the incinerator staff to quench the residue just after it emerges from the furnace and before it is transported to its disposal site.

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APPLICABILITY OF EXISTING METHODS FOR THE DETERMINATION OF THE BIOCHEMICAL OXYGEN DEMAND (BOD) OF INCINERATOR QUENCH WATER

A Division of Research and Development
Open-File Report (RS-03-68-18)

written by
Donald L. Wilson, Research Chemist

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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Bureau of Solid Waste Management
1970

Summary of BOD-Quench Water Study

Donald L. Wilson

An investigation was undertaken to determine if commonly used procedures for BOD determination in water pollution control were applicable to incinerator quench waters.

Personnel in water pollution control are employing DO meters, calibrated using the Alsterberg (Azide) Modification of the Winkler Method. The DO meter commonly used is produced by the Weston and Stack Company.

Although the Weston and Stack (DO) Analyzer was found applicable in determining BOD of incinerator quench water, quick qualitative tests were established which would determine if the Azide Modified Winkler Method is also applicable. These qualitative test are for those who do not have a DO meter and do not wish to buy one unless their particular samples require one. It is thought that only in rare instances could the Winkler (Azide) Method be employed to determine BOD of incinerator quench water.

Since the DO Analyzer may be used in the field where comparison of the Analyzer to the Modified Winkler Method may be difficult, a procedure for an easy field check on the analyzer's performance was developed. In this field-operation-check method, each analyst must determine the Δ ppm value for his particular instrument while the instrument is functioning correctly. This field-operation-check method does not and was not meant

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to replace the actual calibration procedure involving the upper point, with sample at saturated oxygen concentration and the lower point, with sample at zero oxygen concentration.

Quench water samples were found to have BOD values (5-day basis) ranging about from 100 to 300 ppm. The samples normally required a dilution factor of 40 or 2.5 percent dilution; however, whenever possible the analyst should employ more sample in order to reduce the possible error in the BOD result. No modifications of existing methods were found necessary, however, the seeding technique or the immediate DO analysis are not recommended. Seeding requires some knowledge of the organisms present in the samples. Therefore, finding the appropriate seeding material for quench water would be very difficult. Immediate DO demand is sometimes employed to separate biological from chemical demand. But, the immediate DO demand test is difficult to perform at an incinerator site and the chemical effects upon the immediate test cannot be minimized by the aeration step which is performed on all samples in the 5-day test.

Much of this investigation dealt with concepts already verified, therefore, statistically sufficient data to prove each statement was not required in this study.

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REPORT ON THE APPLICABILITY OF EXISTING METHODS FOR THE DETERMINATION OF THE BIOCHEMICAL OXYGEN DEMAND (BOD) OF INCINERATOR QUENCH WATER

Donald L. Wilson*

Abstract

For many years the Alsterberg (Azide) Modification of the Winkler (Dissolved Oxygen) Method has been used for the determination of the Biochemical Oxygen Demand (BOD)** of water samples from lakes, rivers, streams, sewage, and industrial waste waters. When this procedure was employed, to characterize incinerator quench water*** many interferences were encountered. Many of the interfering substances found in quench water are also in those water samples mentioned above but in lower concentrations. This report describes the analytical problems created by interferences and demonstrates how they may be overcome using a dissolved oxygen analyzer. Since such an instrument may not be available in every laboratory, this summary also discusses some qualitative tests for interferences and under what circumstances the Alsterberg (Azide) Modification of the Winkler Method may be employed.

Using 5-day BOD basis, incinerator quench water samples normally had BOD values ranging about from 100 to 300 ppm. A dilution factor of 40 or 2.5 percent dilution (25 ml of sample diluted to one liter) was usually

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**The BOD test is essentially a bio-assay of oxygen loss during standardized incubation.

***In this report quench water refers to that water which has been employed by the incinerator staff to quench the residue just after it emerges from the furnace and before it is transported to its disposal site.

employed with these samples. With the above restrictions, the readability of the apparatus will not afford BOD values below 23.5 ppm or 54.1 ppm. DO Analyzer or Modified Winkler Method, respectively.

Introduction

During the quenching of incinerator residues, the water becomes contaminated with large amounts of living organisms. To determine the biological metabolism in this polluted water, the analyst performs a biochemical oxygen demand test which measures the amount of dissolved oxygen required for oxidation of the organic matter by microbial action in the presence of oxygen.

The oxygen demand of incinerator quench water (or similarly contaminated water) is exerted by three classes of materials: (a) carbonaceous organic material usuable as a source of food by aerobic organisms; (b) oxidizable nitrogen derived from nitrite, ammonia, and organic nitrogen compounds which serve as food for specific bacteria (e.g., Nitrosomonas and Nitrobacter Species); and (c) certain chemical reducing compounds (e.g., ferrous iron, sulfite, and sulfide) which will react with molecularly dissolved oxygen. Since the oxidation of nitrogeneous materials may proceed at a variable rate, even delayed for several days unless suitable micro-biota are available, the nitrification process is usually inhibited. In this study, nitrification was inhibited by the recommended pH adjustment technique, that is, samples are acidified to pH 2 to 3 and subsequently neutralized (pH 6.5 to 8.3). The inhibition

of the nitrification process restricted the BOD test to the carbonaceous demand and presumedly allowed for a better correlation between BOD values of quench water samples.

Complete stabilization of a given sample, at 20 C, may require a period of incubation too long for practical purposes. For this reason, the 5-day period has been accepted as the standard time for BOD analysis. Conversion of data from this incubation period to another can only be made if oxidation curves (BOD at various incubation periods) have been prepared for the type of samples being investigated.

Approach

Since the DO analysis is an established procedure in water pollution control, some of the scientists familiar with this analysis were consulted. Their recommendations and a literature review suggested that there were only two practical methods, the Alsterberg (Azide) Modification of the Winkler Method[1,2] and a dissolved oxygen analyzer method.

The type of dissolved oxygen analyzer employed in this method development was the recommended Weston and Stack, Model 300.*[3]

The Alsterberg (Azide) Modification of the Winkler Method and the Weston and Stack (DO) Analyzer were employed in determining the BOD of quench waters collected at a local incinerator. By the application of these methods, the analytical difficulties and sample dilutions were revealed.

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* Product (or manufacturer) identification in this report does not imply endorsement by the United States Public Health Service.

Studies were performed to determine if those substances which interfered with the Modified Winkler Method also affected the response of the DO Analyzer. Qualitative tests were developed to detect the presence of these interfering substances. Some of these tests are not element or compound specific but do detect any substance that will behave as the known interfering substances. These tests will enable the analyst to decide if the Modified Winkler Method is applicable to a particular sample.

Since the DO Analyzer may be used in the field, the analyst needs some field method for determining if the analyzer is functioning correctly. Studies were performed to establish a simple field test which (1) would not require as much apparatus as the Winkler (Azide) Method, (2) would not involve gas cylinders or heavy equipment, and (3) would relate more than just one point (as the concentration value for dissolved oxygen with complete saturation at a particular temperature). The field test is not to supersede the regular calibration procedure but to reaffirm that the instrument's linear scale is functioning properly. The approach in this investigation was to find either a medium that had an oxygen solubility value markedly different from that of water or a substance that would react with a definite amount of oxygen in water.

Results

The Alsterberg (Azide) Modification of the Winkler Method was applied to quench water samples collected at the Red Bank Incinerator, Cincinnati, Ohio. All samples were collected at one time, in sterile (no matter

present that contributed to BOD value) plastic containers, and transported immediately to the laboratory where they were promptly analyzed without any pH adjustments to inhibit the nitrification process nor addition of potassium fluoride solution to complex any ferric iron that might be present. The time that elapsed between collection and initiation of analyses was three hours (4 hours is the suggested maximum time without refrigerating sample).

The BOD values of samples, collected from pools in the residue disposal area, range from 107 ppm to 292 ppm (Table 1). Analyses of grab samples of quench water draining from a truck, employed to haul residue to the disposal area, always yielded erratic results (Table 1).

A dilution procedure using 50 ml of sample diluted to one liter although producing less possible error in BOD results, in our study was unsatisfactory because sometimes less than one ppm of dissolved oxygen was present in the sample after the incubation period (samples 1 and 2 of Table 1). A dilution factor of 40 or 2.5 percent proved satisfactory for the general BOD values (100 ppm to 300 ppm) of quench water. Since duplicate determination did not always agree (one example being Sample #4, Table 1) and the instability of samples usually prevented repeating the (5-day) BOD analysis at a later date (Table 2), triplicate final DO determinations will afford the analyst more assurance in obtaining reasonable duplicate results (usually only duplicate results are reported). Also the BOD test should be initiated within 4 hours after sample collection, however, it is reported that if samples are stored, immediately after collection, at 5C then the initiation of the BOD test may be

delayed up to 24 hours. In order to obtain triplicate BOD determinations (two initial DO and three final DO) with the Modified Winkler Method, two liters of solution (50 ml of sample) is required instead of the normal one liter.

Qualitative tests (Appendix) were employed to analyze these quench water samples for impurities (oxidizing and reducing substances) known to affect the Winkler Method. These tests, when applied to the before mentioned samples, revealed that the samples contained non specific substances that would produce interferences similar to those caused by nitrites, ferric compounds, and sulfites.

Although a pH meter allows more exacting control, ordinary pH paper was believed sufficient to determine the pH of all the samples collected at the Red Bank Incinerator site. The results of this analysis revealed that the quench water samples are basic (pH of 10 to 11) and definitely need a pH adjustment to inhibit the Nitrification process before the BOD analysis is initiated. Besides all samples should be neutralized, if not already, to about pH 7 (pH of 6.5 to 8.3) because of the reported affects upon the incubation period and the Winkler Method of Analysis.

Additional quench water samples were collected from the Red Bank Incinerator for the purpose of (1) studying the effects of sample preparation or alteration upon the BOD results; and (2) comparing the Modified Winkler Method to the DO Analyzer method. All these samples were acquired at one time, in plastic containers (free of substances which have a BOD value). A BOD analysis of a 50 ml to 2 liter-dilution of each sample was

initiated, with and without Nitrification inhibition, four hours after collection. Considering the DO Analyzer to disclose the correct BOD values, the values for quench water (Table 3) were within the 107 ppm to 292 ppm range previously found. The BOD results showed poor precision, between duplicate analyses and duplicate samples, with both the Modified Winkler Method and the DO Analyzer when quench water samples were collected from water draining off a truck loaded with residue (Tables 1 and 3).

The qualitative impurities tests performed on these samples revealed the presence of substances which would affect the Modified Winkler Method. This effect is similar to one produced by samples containing nitrites, ferrous and ferric irons, and sulfates. One sample, which was collected down hill from piles of salt (stored there for icy streets), contained an excessive amount of chlorides. (Although these tests were employed only qualitatively, excess concentration of interferences was easily detected). A later study revealed that, although chlorides do not normally interfer in the BOD test, when an unusually high concentration of chlorides is present in a sample, gas is released during the Modified Winkler Method and the BOD results are affected.

The results of a pH test on these samples again revealed the quench water samples to be alkaline (pH of 10 or 11). Since our tests have indicated (Table 4) and authorities on the BOD test have reported, that pH values other than 6.5 to 8.3 and the Nitrification process can affect the BOD analysis thereby producing unreliable BOD values, all quench water should

be acidified to inhibit nitrification and then neutralized to a pH of 6.5 to 8.3 before the BOD analyses are performed.

After analyzing a number of quench water samples, the pooled standard deviation of the observations by each method (Modified Winkler and Weston and Stack Analyzer) was evaluated. All observations were employed in these calculations except those (1) obtained on samples collected from dump truck drainage and (2) in which less than one ml of titrant was employed in the Winkler titration. In the BOD study of quench water samples from the Red Bank Incinerator, DO data obtained by using the Weston and Stack Analyzer was more reproducible than data obtainable with the Modified Winkler Method (Table 5 and 6).

In order to ascertain that Weston and Stack (or Yellow Springs) Analyzer can better determine DO of quench water than the Modified Winkler Method, impurities, commonly found in contaminated waters and reported to effect the Modified Winkler Method were investigated as to their degree of influence upon each method. One of these impurities is nitrite which when added to water samples (standard BOD dilution medium saturated with oxygen) produced no change in the Analyzers' readings; but, with the Modified Winkler Method produced (above an initial concentration of 4-5 ppm nitrite) an 82 percent increase in DO concentration per ppm nitrite in the 300 ml BOD bottle (Figure 1). Although the Alsterberg Modification attempts to compensate for the presence of commonly found concentrations of nitrites, it clearly cannot be employed in the presence of unusually large nitrite concentrations (greater than 4-5 ppm nitrite in

BOD bottle). (Such high nitrite concentrations could possible exist in water discharged from industrial complex; however, quench water from incinerators is not expected to achieve such high nitrite concentrations).

Nitrite Effect: $2HNO_2 + 2HI \longrightarrow I_2 + 2H_2O + N_2O_2 \longrightarrow 2N_2O_2 + 2H_2O + O_2 \longrightarrow 4HN_2$

Evaluation of the effect of sulfite solution upon the DO determination revealed almost no change (only about 0.4 percent per ppm sulfite because of oxygen depletion) in the DO Analyzers' readings while the Modified Winkler Method showed a decrease, in dissolved oxygen analysis, of 5.5 percent per ppm sulfite in 300 ml BOD bottle (Figure 2).

The sulfite effect upon the Modified Winkler Method is linear and, if the sulfite concentration of a sample is known, a correction factor could be applied to the BOD value; however, the true sulfite effect may not be known because in highly alkaline conditions, as in the Winkler Method, polythionates and similar organic sulfur compounds break down to form sulfites and thiosulfates,[5] thus increasing the total sulfite effect.

Sulfite Effect: $Mn(OH_2) + 3H_2SO_3 + 2O_2 \longrightarrow Mn(SO_4)_2 + H_2SO_4 + 3H_2O$

When the addition of iron was investigated, the DO Analyzers were not affected; but the Modified Winkler Method showed a decrease in dissolved oxygen analysis. This decrease was about 0.7 percent per ppm ferrous iron in the 300 ml BOD bottle (Figure 2). Ferric iron had no effect upon the method until at least 50 ppm of ferric iron was placed in the BOD bottle. Then the Modified Winkler Method showed an increase of 2.3 percent in the DO value. After 100 ppm (total) of ferric iron was added to the BOD bottle, a DO value increase of 3.1 percent was observed.

As with the sulfites, analyzing a sample for the amount of ferric and ferrous iron present will now allow a correction factor to be applied to the BOD value. The effect of each iron salt varies because several possible reactions are involved and each of these reactions does not go to completion.[6]

Ferrous Effects: $Fe^{+2} + O_2 \longrightarrow Fe^{+3}$

$$2Fe^{+2} + I_2 \longrightarrow 2I^{-} + 2Fe^{+3}$$

Ferric Effects: $FeCl_3 + 2NaI + Na_2S_4O_6 \longrightarrow I_2 + 2Na_2S_2O_3 + FeCl_2 + Cl^{-}$

$$2Fe^{+3} + 2I^{-} \longrightarrow I_2 + 2Fe$$

Since the Modified Winkler Method is still employed to calibrate the DO Analyzers, some aspects of the method were investigated. Stability of the sodium thiosulfate solution and variation in its standardization procedure could ultimately affect the BOD results. Tests showed that a solution of sodium thiosulfate (chloroform added as a preservative) is stable for, at least, 14 days and may be standardized using either the potassium dichromate method or the biniodate method (Table 7).

The Weston and Stack Analyzer may be used in the field where comparison of the Analyzer (recently calibrated) to the Modified Winkler Method may be difficult. The development of an easy field calibration or check on the Analyzer's performance involved investigating various materials (Table 8). None of the mediums evaluated had an oxygen solubility which vary measurably from water and thus satisfactory for a field calibration check. Efforts were, therefore, directed to finding a substance which would react with a definite amount of dissolved oxygen and provide a simple field

operation check of the Weston and Stack Analyzer.

Several substances tried produced a detectable but non-reproducible change in the oxygen concentration. Only those substances which showed a good measureable change in the dissolved oxygen value are discussed herein. One such substance was sodium sulfite (regularly used to zero DO meters). However, the reaction of sodium sulfite with the dissolved oxygen does not come to an equilibrium stage since all the dissolved oxygen loss is so great and varies so immensely with only small differences in the weight of sodium sulfite employed that attempting to measure this rate of loss is impractical (Figures 3 and 4).

At first glance, Oxsorbent®, obtained from the Burrell Corporation, showed great promise as a substance for the field operation check procedure. Good reproducible data was obtained when a syringe was used to measure the Oxsorbent®. However, additional tests revealed that the capability of Oxsorbent® to remove dissolved oxygen from samples decreased greatly when the Oxsorbent® reagent was momentarily exposed to the air.

The most promising results were obtained with the combination of 2 ml and 0.25 M manganese sulfate and 2 ml 0.50 M potassium hydroxide. One ml of each solution produced too slow and too small a DO change (initial DO of 9.20 ppm changed to 7.85 ppm after 10 minutes, sample temperature 24.0C) while two ml of manganese sulfate solution and four ml of potassium hydroxide solution produced too great and too rapid a DO change

(initial DO of 9.15 ppm changed to 1.80 ppm in 15 minutes, sample temperature 24.2C). Using a syringe, instead of a pipet, to measure these reagents did not improve the reproducibility of data. The procedure, employing 2 ml of each solution, was applied in 17 trials with a 10-minute reaction period and in 18 trials with a 15-minute reaction period, sample temperature range 23.6C to 25.9C. The standard deviation of the field operation check method, whether using a 10 or 15 minute reaction period, was 0.20 (Table 9). These tests were conducted with the same membrane on the DO probe. When a new membrane was installed and the field operation check performed twice in triplicate, the change in DO during a 10-minute reaction period averaged 3.85 ppm, sample temperature 25.8C. The mean Δ ppm value (3.60) and the standard deviation value (0.20) of the proposed 10-minute test are dependent upon the particular instrument involved and any large differences between temperatures of samples; therefore, the analyst should establish the Δ ppm value for his own instrument and in the desired sample temperature span before employing it in the field. However, mean Δ ppm values obtained under various conditions are not expected to differ greatly from our mean value of 3.60 ppm.

In a simulated field evaluation, a triplicate field operation check required approximately 35 minutes. This time represents the maximum interval and is greatly reduced by performing the triplicate 10-minute test simultaneously. In any event, the field operation check requires less time than a complete calibration check involving the Modified Winkler Method.

Conclusions

When properly interpreted, biochemical oxygen demand measurements can serve as an index to water quality. The Alsterberg (Azide) Modification of the Winkler Method proved to be an unsatisfactory method for determining these measurements on the quench water samples tested. However, before purchasing a DO analyzer the analyst can, if he so desires, judge for himself the applicability of the Modified Winkler Method by performing some quick qualitative tests (appendix) on his particular samples.

The Weston and Stack DO Analyzer, Model 300-B, successfully analyzed quench water samples for their BOD content and a detailed method was written for the application of this instrument. Included in this detailed method is the newly developed procedure for an easy and quick field calibration check on a properly calibrated DO Analyzer.

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I. Tables and Figures

TABLE I

APPLICATION OF ALSTERBERG (AZIDE) MODIFICATION OF THE WINKLER METHOD TO QUENCH WATER

Sample Nos.	Exact site of collection	ml of sample diluted to one liter	5-day BOD[a] (ppm)
1	Pool of water in residue disposal area	50	156 156
2	Same	50	148 154
3	Same	25	248 227
4	Same	25	127 292
5	Same	10	117 107
6	Water draining from trucks, just filled with residue	50	11.2 11.0
7	Same	50	12.6 9.6
8	Same	10	383 203
9	Same	10	325 198
10	Same	5	24.0 12 4

[a] Each sample had one initial DO and two final DO. The two final DO values permitted duplicate BOD results to be reported.
Example: sample #2, initial DO of 10.05 minus final DO values of 0.91 and 0.50 yielded duplicate BOD results of 7.41 ppm and 7.72 ppm. These results times a dilution factor of 20 equaled BOD values of 148 ppm and 154 ppm for the original sample.

TABLE 2

EFFECT OF SAMPLE AGE UPON BOD RESULTS[a]

Sample[b] Numbers	BOD, ppm (5 day basis)		
	Determinations initiated 3 hours after collection (Modified Winkler Method)	Determinations initiated 15 days after collection[c]	
		Modified Winkler	DO Analyzer
1	127	49.2	23.6
	292	46.4	9.6
2	383	331	59.6
	203	330	49.6
3	325	316	57.6
	198	311	77.6
4	24.0	321	103.6
	124	293	65.6

[a] Since a DO analyzer was not available during all of the study, a complete comparison of these results with those of a DO analyzer could not be made.

[b] These examples were also used in Table 1 and did not show good agreement.

[c] Samples stored at room temperature during aging. Values expected to be about 100 ppm to 300 ppm. Assuming DO Analyzer values are correct, comparing values obtained with the two methods indicates the BOD data employing the Modified Winkler Method is affected by impurities present in quench water samples.

TABLE 3

BOD DETERMINATIONS PERFORMED WITH THE ALSTERBERG (AZIDE) MODIFICATION OF THE WINKLER METHOD AND THE WESTON AND STACK DO ANALYZER, MODEL 300-B

Sample Numbers	Exact site of collection	BOD, ppm	
		Modified Winkler	DO Analyzer
1[a]	Tap water just before quenching process	2.41 3.45	0.15 0.00
2[b]	Water draining from truck employed to haul quenched residue	119.2 44.6	155.0 112.0
3	Sewer directly under residue hopper	150.8 141.6	166.4 168.0
4[c]	Pool between residue disposal area and loading zone.	36.0 27.6	143.4 149.0

[a]Although not a quench water sample, the BOD results of this sample represent the possible amount of BOD value that could be contributed by the water being employed. However, when the Modified Winkler Method is employed, the results indicate the value obtained may be due to interferences only.

[b]Although previous shown with the Modified Winkler Method in Table 1, this sample was analyzed to show that with either method samples from this source generally yield BOD data with poor agreement.

[c]Based upon a definite positive result to a qualitative test, this sample contained an excessive amount of chlorides.

TABLE 4

EFFECT OF NITRIFICATION INHIBITION
AND pH ADJUSTMENT UPON BOD ANALYSIS

	BOD, ppm[a]			
	Before Inhibition and pH Adjustment		After Inhibition and pH Adjustment (6.5 to 8.3)	
Sample Nos.	Modified Winkler	DO Analyzer	Modified Winkler	DO Analyzer
1	119.2	155.0	132.8	130.4
2	150.8	166.4	129.2	126.8
3[b]	36.0	143.4	4.4	93.6
4[c]	27.2	0.0	2.0	0.0
5[d]	35.6	8.2	35.0	30.0
6[e]	23.8	0.0	12.2	10.8

[a]Data obtained with the Modified Winkler Method are not to be compared with data of the DO Analyzer Method and such data does not exclude the possibility of effects from other parameters.

[b]This example is the same sample employed as example 4 in Table 3 and reportedly contains excessive amount of chlorides.

[c]This is same sample as example number 3, except the determination was initiated 8 days after collection. (Comparing examples 3 and 4 is another example of effect of sample's age upon the BOD results).

[d]Not a quench water sample; however, this sample still illustrates the effects in question upon the BOD analysis. This is a well mixed sample consisting of the dilution-water-medium normally employed in the BOD test and relatively large amounts of soil.

[e]Not a quench water sample. This sample was decanted from a water-soil mixture (example no. 5) after most of the soil was allowed to settle.

TABLE 5

DO ANALYSIS

Type of Method Employed	Number of Determinations	Pooled Standard Deviation
Weston and Stack Analyzer	82	0.21[a]
Modified Winkler	76[b]	0.49

[a]The absolute value of the difference between duplicated readings should not exceed $1.96\sqrt{2}$ s, or 0.58 ppm, more than 5% of the time.

[b]Samples with less than one ml titrant were omitted.

TABLE 6

BOD ANALYSIS

Type of Method Employed	"S"[a] or $\sqrt{s^2+s^2}$	Dilution Factor[b]	Confidence Range[c] or ± (S) (1.96) (40)
Weston and Stack Analyzer	0.30	40	± 23.5
Modified Winkler	0.69	40	± 54.1

[a] "S" is an estimate of the standard deviation of differences between two DO readings (i.e., a single BOD result).

[b] Dilution factor may vary but for calculation purposes the normal dilution factor is shown here.

[c] 95% confidence limits about a single BOD result, assuming a standard dilution factor of 40 or 2.5 percent dilution.

TABLE 7

STABILITY AND STANDARIZATION OF
SODIUM THIOSULFATE SOLUTION

Solution	Age of Solution (days)	Method of Standardization	Normality[a] (approx. 0.025)
1	0	potassium dichromate	0.0249
	9	potassium dichromate	0.0248
	14	potassium dichromate	0.0246
2	1	potassium dichromate	0.0248
	3	potassium dichromate	0.0247
	6	potassium dichromate	0.0248
3	1	potassium dichromate	0.0245
	1	biniodate	0.0247
	2	biniodate	0.0246
	5	biniodate	0.0248
	5	potassium dichromate	0.0247

[a]Each normality value is the average of 2 to 4 determinations.

TABLE 8

MATERIALS EVALUATED IN THE DEVELOPMENT OF A PROCEDURE FOR THE FIELD CALIBRATION AND OPERATIONAL CHECK OF THE WESTON AND STACK DISSOLVED OXYGEN ANALYZER, MODEL 300

Column A	Column B
Mediums having an oxygen solubility different from that of water	Substances that may react with a definite amount of oxygen, dissolved in water
Ethyl alcohol	Aspirin
Acetone	Sodium sulfite, solid and in solution
Glycerin	Potassium iodide
Prestone®	Sodium nitrite
Ethylene glycol	Ferrous ammonium sulfate
Ethylene glycol with various amounts of water	Oxsorbent®
Methyl alcohol	Potassium iodide-sulfuric acid
	Potassium iodide-sulfuric acid-ferrous sulfate
	Sodium thiosulfate
	Cupric sulfate
	Magnesium sulfate
	Potassium permanganate
	Potassium dichromate
	Manganese sulfate-potassium hydroxide, solid and in solution

TABLE 9

REPRODUCIBILITY OF DATA OBTAINED IN THE PROCEDURE FOR THE FIELD OPERATION CHECK

Statistic	Change in DO reading[b]	
	10 Minute Reaction period	15 Minute Reaction period
Arit. Mean[a]	3.60	3.75
Std. Dev.	0.20	0.20
Confidence Limit	±0.10	±0.10

[a]Based upon triplicate observations

[b]Results are based upon our particular instrument and a definite temperature range (23.6C to 25.9C).

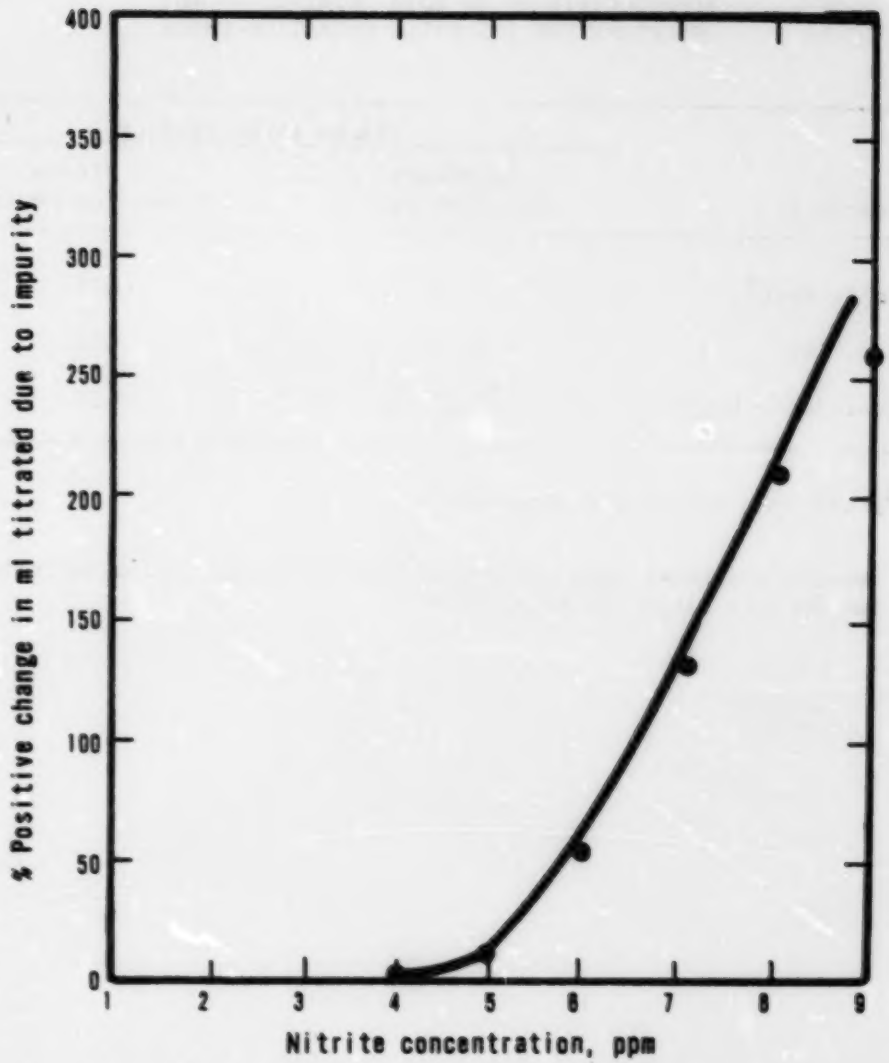

Figure 1. EFFECT OF NITRITE CONCENTRATION IN "QUENCH WATER" SAMPLES UPON DO ANALYSIS BY MODIFIED WINKLER METHOD.

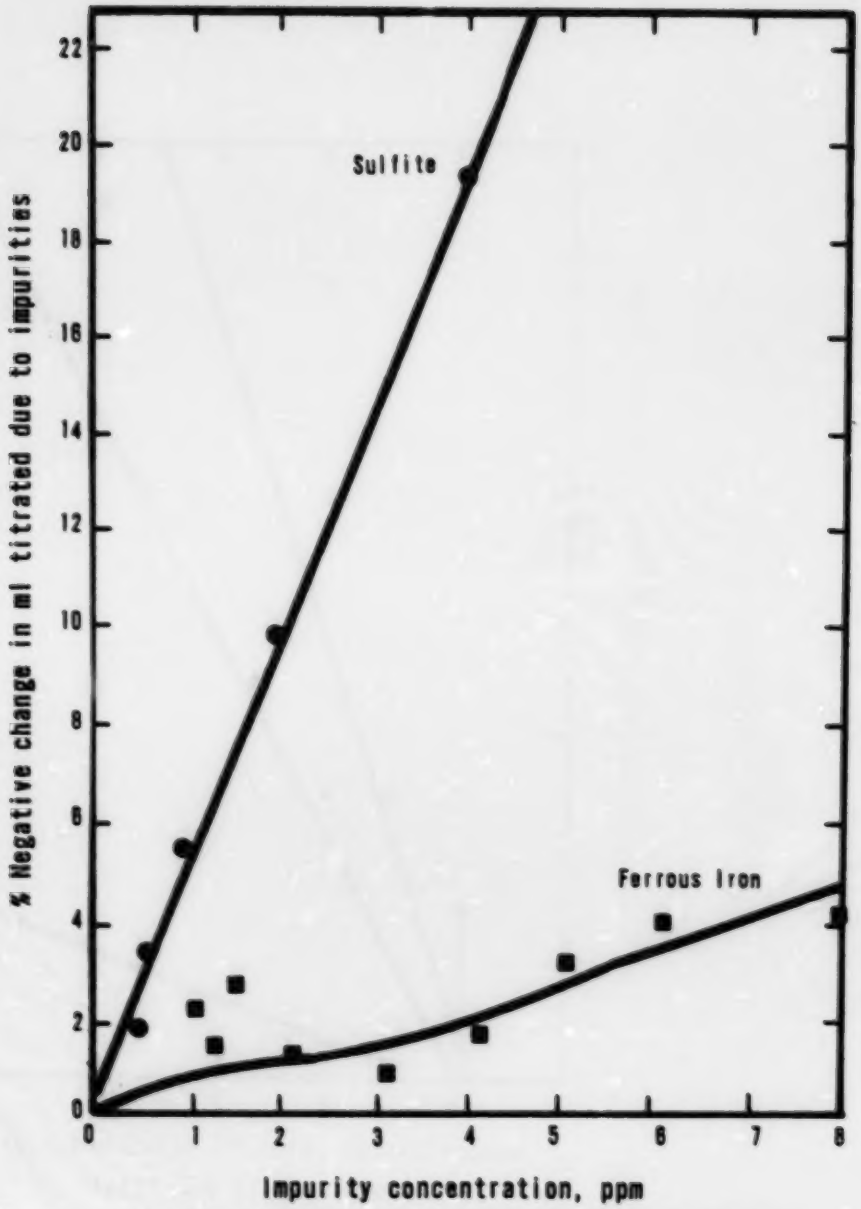

Figure 2. EFFECT OF SULFITE AND FERROUS IRON CONCENTRATIONS IN "QUENCH WATER" SAMPLES UPON DO ANALYSIS, USING MODIFIED WINKLER METHOD.

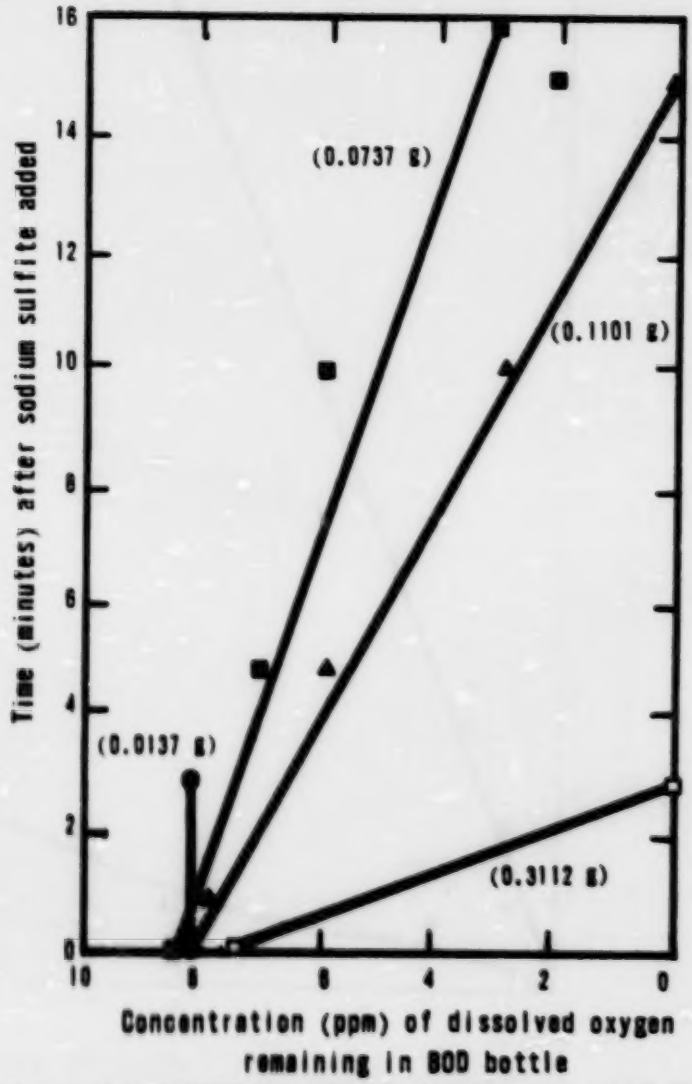

Figure 3. EFFECTS OF VARIOUS WEIGHTS OF SODIUM SULFITE ON DO DEPLETION IN WATER SAMPLES.
(Sample temp. 24°C)

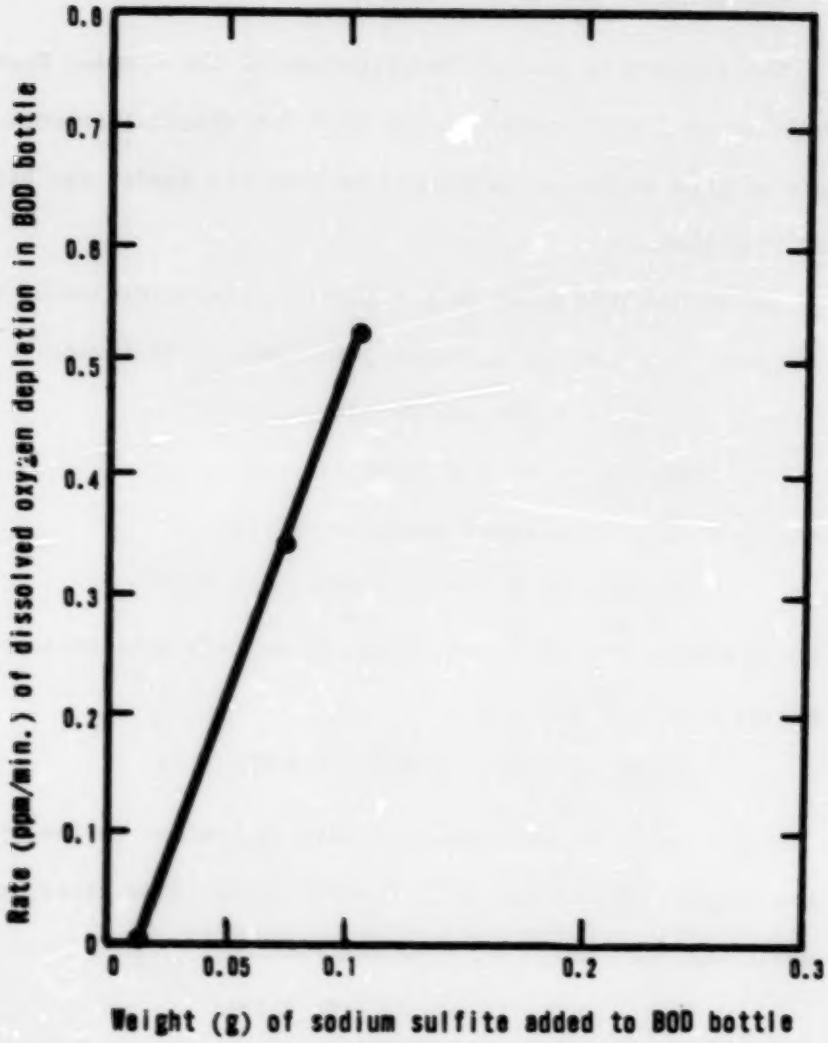

Figure 4. RATE OF DO DEPLETION IN WATER SAMPLES PRODUCED BY VARIOUS WEIGHTS OF SODIUM SULFITE.

II. MECHANISM OF ALSTERBERG (AZIDE) MODIFICATION OF THE WINKLER METHOD

The Alsterberg (Azide) Modification of the Winkler Method employed in this study has not been altered from its original concept. The mechanisms of this method is presented so that the reader may better understand this report.

The Modified Winkler Method involves the oxidation of manganous by the oxygen, dissolved in the water, to manganic hydroxide:

$$MnSO_4 + 2\ KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

Which, when acidified, forms manganic sulfate.

$$MnO(OH)_2 + 2H_2SO_4 \longrightarrow Mn(SO_4)_2 + 3H_2O$$

In the presence of iodide, the manganic sulfate acts as an oxidizing agent, releasing free iodine.

$$Mn(SO_4)_2 + 2KI \longrightarrow MnSO_4 + K_2SO_4 + I_2$$

The latter, which is stoichiometrically equivalent to the dissolved oxygen in the sample, is titrated with 0.025N sodium thiosulfate, in the presence of starch or Thyodene, to a blue end point.

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

One ml of 0.025N sodium thiosulfate is equivalent to 0.200mg of dissolved oxygen or if 200 ml of original sample is titrated one ml of titrant is equivalent to 1 mg/l (ppm) DO.

$$Na_2S_2O_3 \equiv I_2 \equiv Mn(SO_4)_2 \equiv MnO(OH)_2 \equiv O_2$$

The Alsterberg (Azide) Modification of the Winkler Method utilizes sodium azide to reduce nitrites which are commonly found in polluted waters and interfere in the analysis.

Without sodium azide:

$$2HNO_2 + 2HI \longrightarrow I_2 + 2H_2O + N_2O_2$$

$$2N_2O_2 + 2H_2O + O_2 \longrightarrow 4HNO_2$$

With sodium azide:

$$NaN_3 + H_2SO_4 \longrightarrow NaHSO_4 + HN_3$$

$$HN_3 + HNO_2 \longrightarrow N_2 + N_2O + H_2O$$

III. MECHANISM OF WESTON AND STACK (DO) ANALYZER

The Weston and Stack Analyzer, Model 300, is ruggedly constructed, moisture-proof, and portable. Its probe is constructed of cast-epoxy and is separated from the sample by a Teflon membrane through which the gases, dissolved in a sample, can diffuse. The probe is specially designed to fit into standard BOD bottles and has a built-in agitator which produces a precise and constant degree of sample turbulence. Within the probe is a pair of electrodes surrounded by a solution of electrolyte, potassium iodide.

The oxygen, dissolved in the sample, is reduced at the platinum electrode cathode:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

by the $^-$o.578 voltage which results from the cell's potential energy. Hydroxide ions flow through the electrolyte and react with the lead anode:

$$Pb + 4OH^- \longrightarrow PbO_2^{=} + 2H_2O + 2e$$

to produce a flow of electrons. The signal from the probe is directed to an operational amplifier in the readout instrument. The meter is calibrated so that each meter readout unit is equivalent to one ppm (mg/ℓ) of dissolved oxygen in the sample. Changes in the oxygen diffusion rate due to temperature variation is compensated for by special electronic features of the analyzer. The instrument is calibrated in a medium similar to the final sample medium to prevent any change in diffusion rate produced by dissimilar conditions.

IV. QUALITATIVE TESTS FOR IMPURITIES

These tests may be employed as a quick means of detecting the presence of oxidizing or reducing substances which will interfere with the Modified Winkler Method for the determination of BOD.

Although sulfate does not affect the Modified Winkler Method, the presence of large quantities of it may indicate the possible presence of sulfite which definitely affects this method. Sulfate is generally detected [1] by adding a portion of barium chloride solution (about 10g to 500 mℓ) to the sample. A cloudy white solution indicates substances like sulfate and/or sulfite are present.

Substances, similiar in effect to sulfite, can be detected by following a procedure similar to the method employed to standardize the sodium thiosulfate solution utilized in the Modified Winkler Method. A small amount of a potassium iodide solution (2 g to 200 mℓ, plus 10 mℓ conc. HCl, to final vol. of 250 mℓ-prepared day to be used) is added to

the sample. A cloudy white or yellow (color appears after 1 to 2 minutes) solution indicates that interferences like thiosulfate are present. However, if the mixture remains clear, sulfite-like interferences may still be present. Add a small amount of Thyodene powder to the clear mixture and to a small amount of the potassium iodide solution (may turn pale blue). Then with both solutions perform a dropper-titration using potassium dichromate solution (2g to 500 mℓ) as the titrant. The potassium iodide solution should turn the yellow color of the dichromate solution with only 1 to 2 drops of titrant. If even only one ppm of sulfite-like material is present in the sample solution, the solution will turn blue with only 1 to 2 drops of titrant and several drops will be needed before the sample solution has the yellow color of the dichromate solution. The presence of sulfite-type substances in a sample can produce false negative results with the tests for interferences similar to nitrite, ferrous iron, ferric iron, and residual chlorine in effects. However, since no amounts of sulfite-type materials can be present in a sample, a positive test for these materials eliminates the need in performing other tests.

Since nitrite, above 5 ppm in BOD bottles, will interfere with the Modified Winkler Method, the analyst must detect its presence if he wishes to use this method for BOD analysis. The test for nitrites described here is an adaptation of a procedure developed by Saltzman.[2,3] This test involves the addition of a small amount of test solution (10 m acetic acid, 10 g sulfanilic acid, 1g 1-naphthylamine hydrochloride, dissolved and diluted to 250 mℓ) to the sample. A red color produced by an azo dye indicates that substances similar to nitrite are present. A comparison of the

red color to that color produced by a nitrite standard will show the approximate amount of nitrite-type substance present.

Interferences, as ferrous iron, can be detected by adding a portion of 1,10 phenanthroline solution (5g to 500mℓ) to the sample.[4] After a few minutes, an orange-red complex will indicate the presence of substances similar to ferrous iron in effect.

Since very large amounts (50 ppm or more in BOD bottle) of ferric iron or similar substances can also affect the Modified Winkler Method, the presence of these substances must be determined. The method for this determination involves the addition of a small amount of hydroxylamine solution (5g to 500mℓ) to the sample portion, previously tested for ferrous iron. After a few minutes the formation of a deeper orange-red complex indicates the presence of ferric-iron-type materials. A comparison of this color with the color produced by a ferric iron standard solution will indicate the approximate concentration of ferric-iron-type substances in the sample.

Since residual chlorine, another interfering substance, dissipates when samples stand for 1 to 2 hours or they are well aerated, a test for residual chlorine and similar gases was not established. However, since these gases can be created during the Modified Winkler application, a test for their possible creation is discussed here. A free-halogen test paper,[5] placed just above the sample while 1 or 2 mℓ of conc. sulfuric acid is added to the sample, will turn blue in the presence of a halogen gas. The test paper is prepared by impregnating ordinary filter paper with a potassium iodide solution (2g to 200mℓ, plus 5mℓ conc. H_2SO_4, to final

volume of 250 mℓ-prepared day to be used).

These qualitative tests are by no means the only tests available. Many tests can be employed but the reader is cautioned that qualitative tests too specific may not reveal what is really desired. Specific tests may give more detailed knowledge about the sample, however these tests may not disclose the presence of all the substances that affect the Modified Winkler Method.

References (for Qualitative Tests)

1. American Public Health Association, Water Works Association, and Water Pollution Control Federation. Sulfate. In Standard Methods for the examination of water and wastewater. 12th ed. New York, American Public Health Association, Incorporated, 1965. p. 287-296.

2. Saltzman, B. E. Colorimetric Microdetermination of nitrogen dioxide in the atmosphere. Analytical Chemistry. 26 (12): 1949-1955, Dec. 1954.

3. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Nitrogen (nitrite). ibid., p. 205-208.

4. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, Phenanthroline Method. ibid., p. 156-159.

5. Feigl, F., Free Halogens. In Qualitative analysis by spot tests. 3d ed. New York, Elsevier Publishing Company, Incorporate, 1946. p. 276.

V. COST OF BOD METHODS

The cost of performing the Alsterberg (Azide) Modification of the Winkler Method was estimated assuming that: (1) the life expectancy of the glassware is five years; (2) two weeks of each year are required for preparation of reagents; (3) eight days per year are holidays; (4) operation will be continuous; and (5) the sample dilution requirements are already known.

The cost of performing the BOD analysis, using the Weston and Stack (DO) Analyzer, Model 300, was estimated assuming that: (1) the life expectancy of the analyzer and membrane is ten years and one month, respectively; (2) two weeks of each year are required for calibration and installation of membranes; and (3) items 3, 4, and 5 for the Modified Winkler Method also apply.

Since an analyst's salary varies with the degree of his training and experience, the geographic location, and type of employment, the yearly cost estimates, presented in the following table, have been reported in terms of labor time.

LABOR TIME AND COST OF EQUIPMENT AND SUPPLIES PER YEAR

Type of method	No. of Samples	Hours required for triplicate determinations	Free time	Cost of chemicals and equip.
Alsterberg (Azide) Modified Winkler	1000	1960	none	$213.10
Weston and Stack DO Analyzer	2000	1960	none	$213.00

These estimates indicate that (1) the time required for the performance of a sample analysis and (2) the cost per sample of materials and equipment is two hours and $0.21 for the Modified Winkler Method and one hour and $0.11 for the DO Analyzer Method.